SEVENTH QUARTERLY REPORT

INVESTIGATION OF ELECTRODE MATERIALS FOR ALKALINE BATTERIES

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TECHNICAL CONTENT STATEMENT

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ABSTRACT

Both AgO and Ag_2O are activated by heat to adsorb oxygen or
some other gas from the atmosphere. The minimum activation
temperature appears to be about 60° for AgO with more effective
activation occurring at higher temperatures. No minimum has been
determined for Ag_2O; however, significant adsorption does occur
on the material. If long periods at 66° are repeated, activation
appears to be increased. At the same time, the weight loss during
heating is greater. This suggests an activation for both ad-
sorption and desorption. On the other hand, repeated short periods
at 66° seem to have an opposite effect as though the material
were being annealed.

The maximum amount of substance adsorbed in the experiments
performed thus far corresponds to about 50 ml of gas for an amount
of AgO equivalent to one ampere-hour.

Preliminary measurements show that the open-circuit poten-
tials of the potassium-amalgam electrode in 9.84 VF KOH range
from about 1.745 V to 1.806 V vs the Hg/HgO reference as the
amalgam concentration ranges from 0.001 to 0.006 AH/g Hg. A slow
drift in the potential is observed with time.

Gold chloride and stannous oxide dissolved in concentrated
KOH are unsatisfactory cathode materials. The copper-amalgam/
cupric ammine system may prove useful as a cathode although the
conductivity of the electrolyte solution is low. The zinc-
amalgam/zincate system shows promise of fairly high discharge rates,
but the open-circuit potential of this cathode combined with the
potassium-amalgam anode is only 0.57 V.

The objectives of the contract are four-fold:

(1) Study of the reduction of Ag(I) by zinc.

(2) Study of the thermal decomposition of AgO and Ag_2O.

(3) Study of the amalgam electrode.

(4) Study of the evolution of gas at electrodes.

This report will be limited to the second and third objectives.

A. THERMAL DECOMPOSITION OF AgO AND Ag_2O

Experimental

The procedure used in these experiments has been largely described in a previous report[1]. All samples were exposed to the laboratory atmosphere throughout the experiments.

Results and Discussion

The experiment which was in progress at the time of the last report[1] was continued. The sample was heated successively at 66°, 76°, and 86° with room-temperature intervals between. No attempt was made to establish constant weight. The results are shown in Figure 1.

The initial slight rise at room temperature is unimportant, probably. Some moisture pickup might be expected, although this has not been observed in most instances. Heating at 66° for about 4 days brought the weight down to 25.620 mg. The sample began to gain weight immediately after the heat was turned off. It should be noted that re-establishment of room temperature required about two hours although the initial temperature drop was rapid. The arbitrary decision was made to heat the sample during each thermal

cycle until the weight had decreased to 25.62 mg.

Several interesting points may be seen in Figure 1. For any given period after the heat was turned off, the amount of material adsorbed increased as the number of thermal cycles increased. In all cases, weights in excess of the original room-temperature weight were obtained during the room-temperature segment of the cycle. The final weight reported in this experiment was approaching a constant value and was 0.360 mg greater than the initial sample-weight; this represents an increase of about 1.5%.

After completion of the set of cycles described above, the temperature of the sample was increased and held at 230° for about 18 hours in order to completely convert the material to Ag_2O. It was assumed that this was accomplished, although no tests were made. The sample was cooled to room temperature and left to stand as before. The results are shown in Figure 2. The total gain in weight on this material was slightly greater than the maximum observed on AgO. The maximum percentage change for AgO was 1.78% and that for Ag_2O was 1.87%. The actual change is not greatly different in the two cases and it may be this quantity which is important here.

A sample of AgO was treated to a modified series of thermal cycles in which the high-temperature portion was held at 66° throughout the experiment and each segment of the cycle was maintained until constant weight was obtained. Constant weight was assumed if the change was less than 5 μg over a 24-hour period. The results are shown in Table 1. Constant weight, as defined

above, had not been attained when the second heating segment was terminated.

The data are sparse and this experiment should be repeated, no doubt. However, 24 days were required to obtain this information and other experiments seemed more important at this time. It is seen that the first loss was comparatively small, being less than that observed in Figure 1. The expected gain above the initial weight was observed on cooling. The results of the second thermal cycle are significant in that the loss was about four-fold greater while the gain was three-fold greater. Thus, repeated thermal cycles appear to increase the adsorption capacity of the material even when the upper temperature is kept the same during the experiment. The increased weight-loss on the second heating also suggests that definite thermal decomposition of the original material is occurring or that there is thermal activation for desorption as well as for adsorption.

A set of experiments is in progress to determine the minimum heating time at 66° that is required to activate AgO. Preliminary data indicate that heating times less than about 8 hours cause very little activation. The last heating period was extended to about 18 hours and there was definite indication of a weight increase at room temperature, although the weight loss during heating was slight. The possibility that some sort of annealing process occurs during repeated short-term heating cannot be discounted. It is also possible that the length of any particular heating period will have a definite effect on subsequent adsorption even though no further weight loss occurs.

A series of experiments was performed to determine the minimum temperature at which the onset of activation occurs. The results suggest this minimum to be about 60°. However, since short periods of heating at this temperature also seem ineffective, it may be that greatly prolonged heating at lower temperatures would ultimately cause activation. This point is probably worth future investigation because it is quite possible for dry-charged batteries to be stored for extended periods at fairly high temperatures; 45° would not be unreasonable in tropical regions. If thermal activation occurred at such temperatures over a long period, the batteries might be expected to gas when put into operation at some later time. If one assumes that the material adsorbed is oxygen, then the maximum observed so far corresponds to about 250 µl on 24.7 mg of AgO. If this is extended to a 1 ampere-hour cell, one might predict release of more than 50 ml of gas--a formidable quantity in the space usually available in a cell.

Proposed Work

Work in progress will be continued. Controlled-atmosphere work (e.g., vacuum, pure oxygen, pure nitrogen, etc.) will begin as soon as possible. Experiments will be extended to Ag_2O samples which have not been prepared through the reduction of AgO. The effect of quantity and dispersion of the sample on the adsorption characteristics will be investigated. It is suggested that long-term activation studies between 25° and 60° be considered.

B. AMALGAM ELECTRODES

Experimental

Attempts were made to measure the open-circuit potential of the potassium-amalgam electrode at various states of charge in 9.84 $\underline{VF}$ KOH. The cell container was a Kontes No. K-25005 Universal Electrode Holder which consists of a 125-ml Erlenmeyer type flask with vertical side-arms attached opposite each other near the bottom. These side-arms are constructed with standard-taper joints so that electrodes can be inserted while maintaining a controlled atmosphere within the flask. The opening to the flask (center section) was a standard-taper female joint and was equipped with a Teflon stopper through which a glass tube could be inserted.

The reference electrode, an Electrochemical Research Associates Hg/HgO electrode in 20% KOH, was inserted in one side-arm. The electrode has a potential of 0.098 V $\underline{vs}$ SHE. Nitrogen was passed into the cell through the other side-arm. About 2.2 g of Hg for the amalgam electrode was contained in a Kontes No. K-25605 Amalgam Electrode Holder mounted in the center section of the cell with contact being made through the hole in the Teflon stopper. The complete unit was mounted in a water bath controlled at 24.6°.

Measurements were made with a Leeds and Northrup K-3 potentiometer and Leeds and Northrup Model 2430-C guarded galvanometer. Because the voltage of the complete cell exceeded the

range of the potentiometer, a battery of accurately known voltage
was placed in the circuit to balance part of the amalgam-cell
voltage. The mercury cell initially used for this purpose was
found to be too unstable and it was replaced with an Eppley
Student's standard cell.

The electrolyte solution in the cell was swept with nitrogen
which had been passed through a bubbler train containing a
vanadous solution[2] to remove oxygen. The cell was allowed to
reach temperature equilibrium with the bath before the amalgam was
charged. The counter electrode for the charging process was a
platinum wire mounted in the side-arm containing the nitrogen
inlet.

Solutions of various substances which seemed to show promise
as cathode materials were tried. These substances were dissolved
in concentrated base and placed in contact with a mercury pool.
The resulting electrode was "discharged" by passing a current from
a constant-current power supply through the system[1].

The zinc-amalgam electrode was charged and discharged at a
hanging drop as previously described[3].

Results and Discussion

The results of measurements of the potassium-amalgam open-
circuit voltage at various amalgam concentrations are shown in
Table 2. These results must be considered preliminary. The drift
indicated in Table 3 is not surprising since the potassium-amalgam
is known to discharge slowly at this KOH concentration. However,
the 3-mV scatter seen in Table 2 seems excessive. Some of these

data were taken using the mercury bucking cell; this might account for some scatter.

The several materials chosen to try as active materials for amalgam cathodes were selected on the basis of their standard potentials[4] and their tendency to dissolve in the electrolyte solution chosen. Most were known to dissolve fairly readily in alkaline solution through the formation of soluble hydroxy-complexes.

Gold chloride, $AuCl_3$, was dissolved in 9.84 VF KOH. In principle, it should be readily reduced to the metal which should amalgamate easily. However, it was found to be too insoluble for our purposes and, furthermore, it oxidizes mercury quite readily. The standard potential suggested this possibility, but it was hoped that the rate would be sufficiently slow that the system could be used.

Stannous oxide is known to be amphoteric and tin should amalgamate. It's potential, although not as favorable as that of gold, should be satisfactory. However, SnO disproportionates rapidly in concentrated alkali to form the metal and SnO_2 which is not soluble. Therefore, this system is not satisfactory. This behavior has been reported in the literature[5].

Gold and silver ammines were discarded since they are known to form dangerously explosive "fulminates". However, copper apparently forms no such substance and is highly soluble in con-centrated ammonia. A cell was constructed using a mercury pool in a $Cu(NH_3)_4^{2+}$ - NH_3 solution. This was "discharged" through a

power supply. Although fairly high current-densities could be obtained--close to 1 A/cm^2--the cell resistance was found to be extremely high. This is probably caused by the fact that ammonia is only slightly dissociated, particularly at the high concentrations used. The concentration of the copper-ammine complex was then insufficient to provide a highly conducting system. In spite of these problems, the copper-ammine system should not be ruled out as an ultimate possibility.

The possibility of the $Zn(OH)_4^{2-}$ - $Zn(Hg)$ - KOH system as a cathode was considered. This would not provide a high cell voltage in conjunction with a potassium-amalgam anode but, if high currents could be obtained, might be usable in a special-purpose battery. The results of a series of charges and discharges are shown in Table 4. Good recovery is obtained at charge and discharge rates of 2,687 mA/cm^2, while less satisfactory though acceptable recovery was obtained at 5,373 mA/cm^2.

A cell was constructed consisting of a $Zn(Hg)$ - $Zn(OH)_4^{2-}$ - KOH half-cell and a K(Hg) - KOH half-cell connected through a salt bridge plugged with glass wool. The complete cell was charged at 5,800 mA/cm^2 and was allowed to discharge through a resistor without application of external power. The maximum current-density obtained on discharge was about 200 mA/cm^2, calculated on the basis of the area of the mercury pool in the Zn(Hg) electrode. This maximum was probably imposed on the system by the high cell resistance. The open-circuit potential was 0.57 V.

Proposed Work

The search for possible cathode systems will be continued. Open-circuit measurements of potential will be made with more potassium- and sodium-amalgam electrodes. Methods for constructing complete amalgam cells will be considered.

Table 1

Adsorption and Desorption of AgO

Temperature was held at about 65° during the heating segment of the cycle and at room temperature during the rest of the cycle. Each segment was continued until constant weight was attained. Gain and loss is expressed with reference to the <u>initial</u> weight at room temperature.

Segment	Gain (μg)	Loss (μg)
1st heat		25
1st cool	55	
2nd heat		105*
2nd cool	160	

*Constant weight not attained.

Table 2

Potassium-amalgam Open-circuit Potentials

Capacity (AH/g Hg)	E_{oc} vs Hg/HgO* (V)
0.001	1.74626
	1.74341
0.002	1.77806
	1.77514
0.003	1.80312
	1.80224
	1.80326
0.004	1.80601
0.005	1.80612
0.006	1.80640

*Potential of Hg/HgO reference is +0.098 V.

Table 3

Potassium-amalgam Open-circuit Voltage Drift

Electrode was charged to 0.003 AH/g Hg

Time	E_{oc} vs $\dfrac{Hg/HgO}{(V)}$
↑ 1 hr ↓	1.78871
	1.78808
	1.78766
	1.78759
0	1.80318
1 day	1.79860
3 days	1.79312

Table 4

Charge and Discharge Characteristics of the Zinc-Amalgam Electrode

Total Charge (A-hr x 10^5)	Current-Density* (mA/cm^2)	Charge Recovery (%)
3.8	1343	96
3.1	1343	100
3.5	2687	95
4.1	2687	95
2.8	5373	84
2.2	5373	77

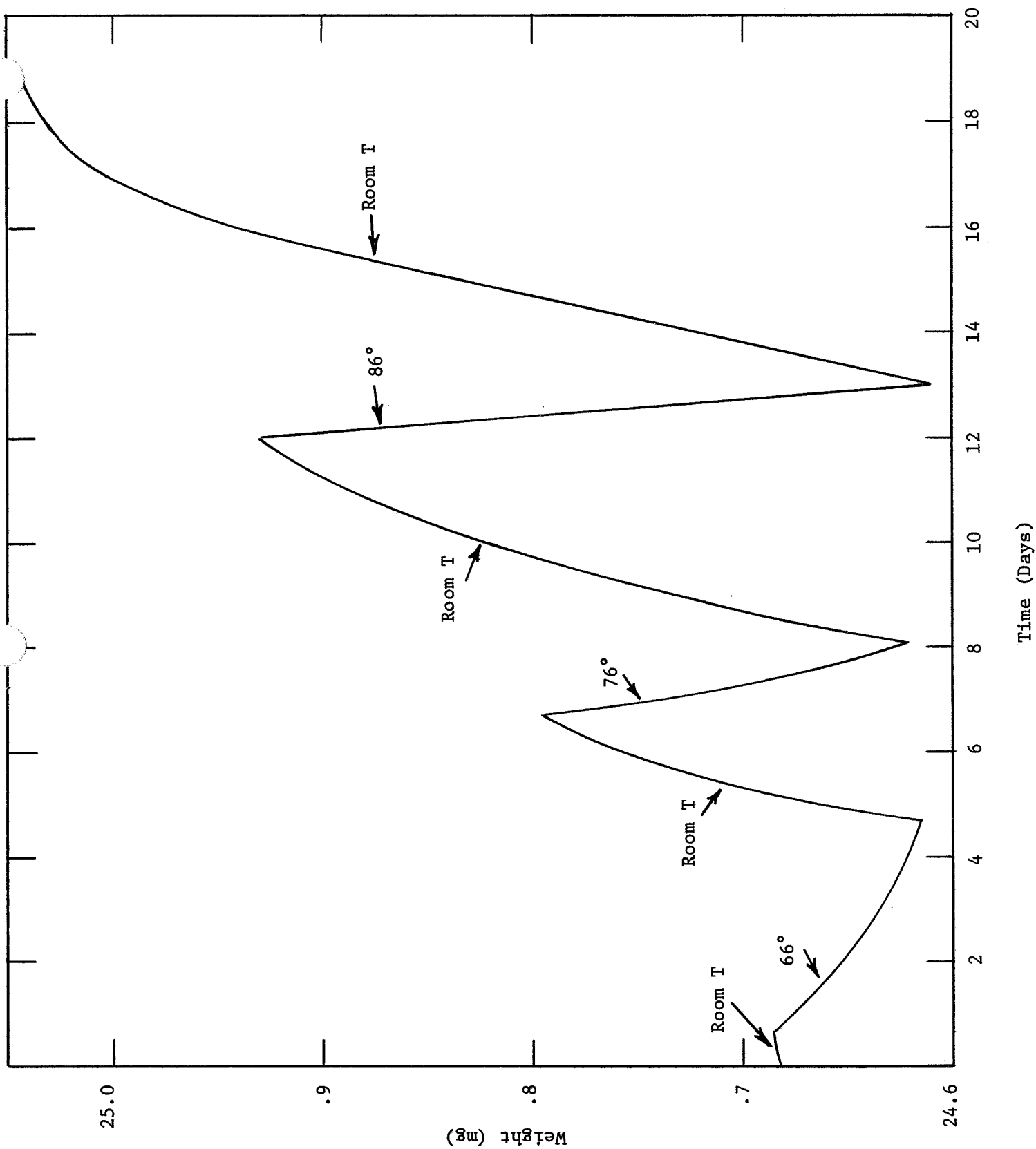* Charge and discharge rates are the same in each run.
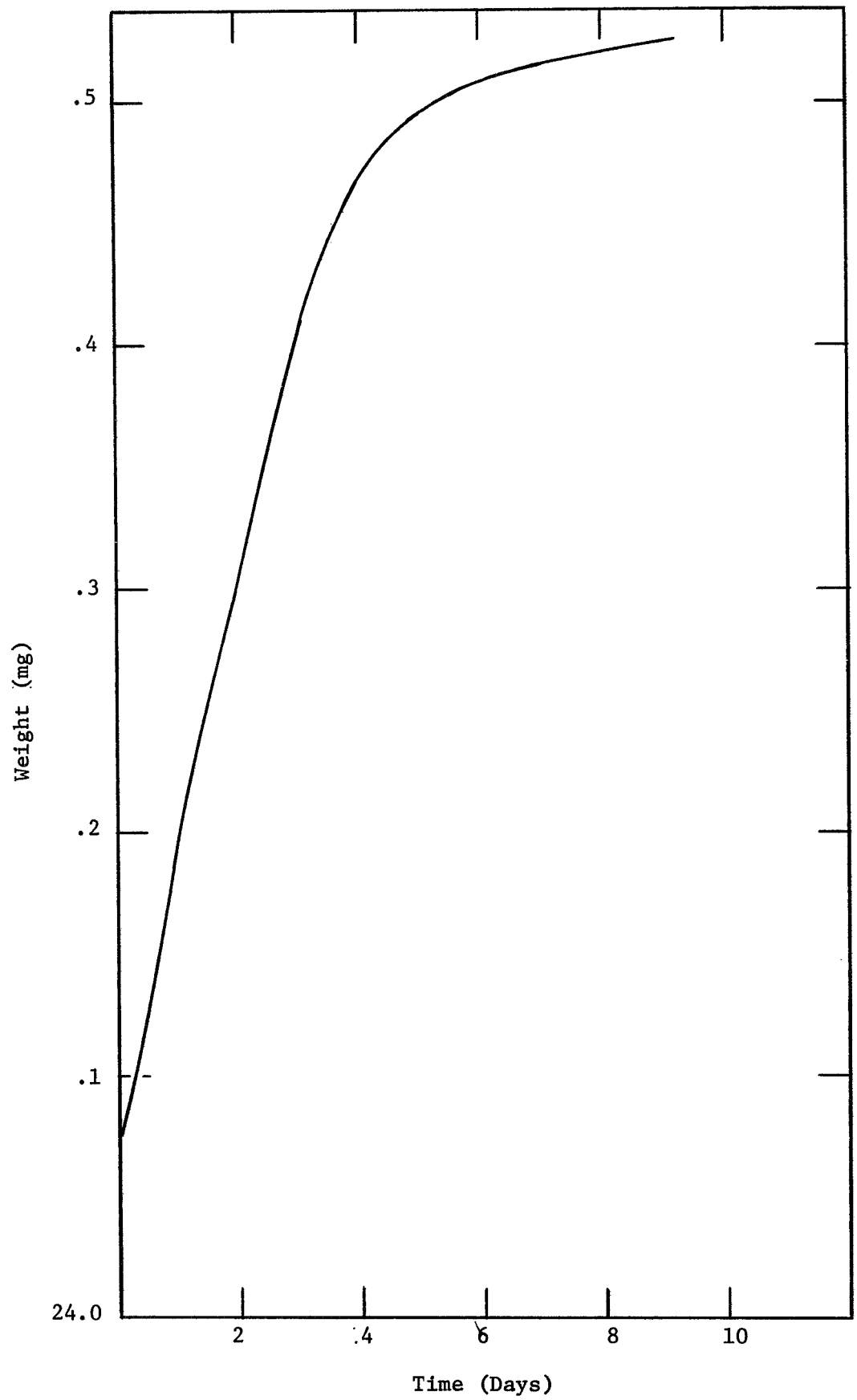
Fig. 1 Adsorption and Desorption on AgO

Fig. 2 Adsorption on Ag_2O

REFERENCES

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